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13. ABSTRACT (Maximum 200 words)

The synthesis of styrene momomer p-vinylbenzoylacetophenone (monomer **1**) has been carried by the acetylation of 2-chloroethylbenzene and base elimination of the resulting 4-acetyl-2-chloroethylbenzene to give 4-acetylstyrene. This monomer was benzoylated by a sodium hydride mediated Claisen reaction with excess ethylbenzoate to give the monomer **1**. This monomer that is of interest in ARO in sensing applications was characterized by proton NMR and by mass spectrometry. Each of the three steps was optimized to give an overall yield of about 35 percent from the starting products. A large amount (50 grams of this monomer) was synthesized and shipped to Dr. Amanda Jenkins.

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Enclosure 1

Report on Research Agreement DAAD19-01-1-0577

Synthesis of New Vinyl Monomers for Chemical Agent Sensing Applications

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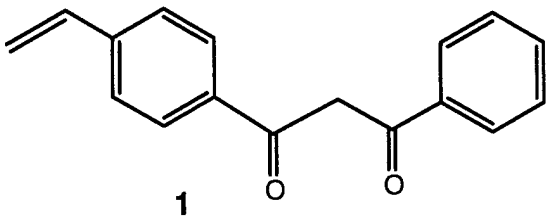
This proposal is being submitted as part of a collaboration with Dr. Amanda Jenkins of the ARO Chemical Sciences Division, Polymer Chemistry Group under the STIR program. The structures of the target monomer ,(**1**) that is of interest with regard to chemical agent sensing and related applications, is shown below. The primary objective was the development of methods suitable for the preparation of multi gram quantities of this monomer. Following the synthetic procedures in Scheme 1, fifty grams of the monomer was prepared over the summer and shipped to Dr Jenkins in September of 2001.



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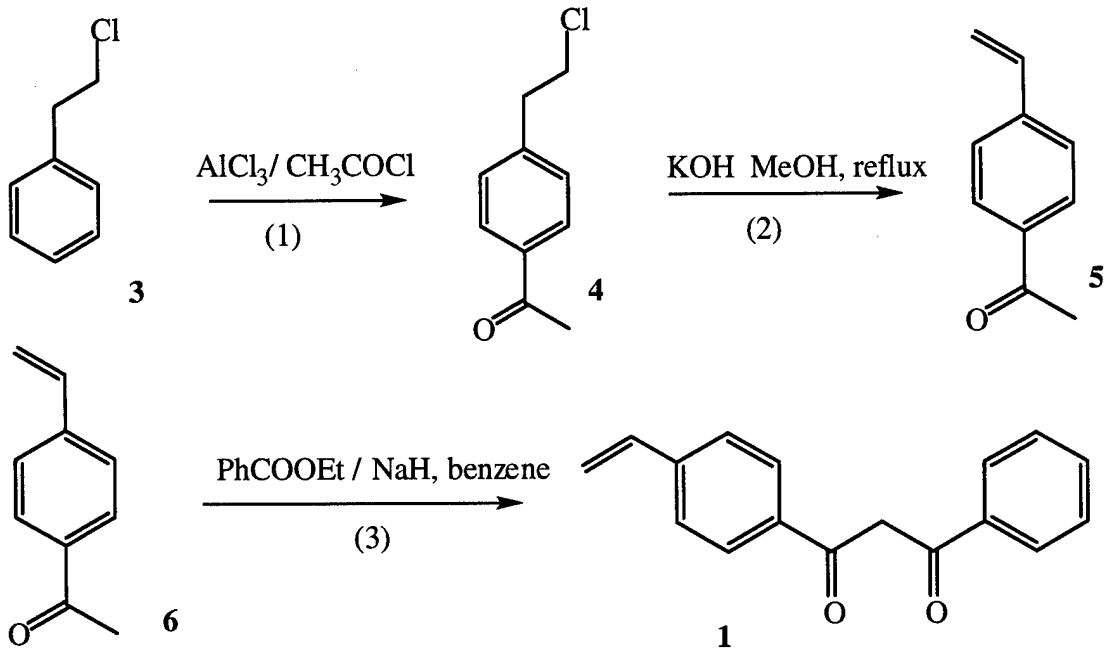
Beyond the interest to the ARO, monomer **1** is intriguing as radical polymerization. is expected to give a polymer with a highly reactive proton that may be removed even by weak bases to give enolate anions that are readily alkylated by a wide variety of electrophiles. As there are two acidic protons per monomer the deprotonation-alkylation procedure may be repeated to give polymers having disubstituted 1,3-diphenyl-1,3-propanedione pendent groups. Furthermore, the monomer may be used for the synthesis of polymer brushes as the malonate type anions may be used to initiate other vinyl monomers.

A. Synthesis of p-vinylbenzoylacetophenone (1)

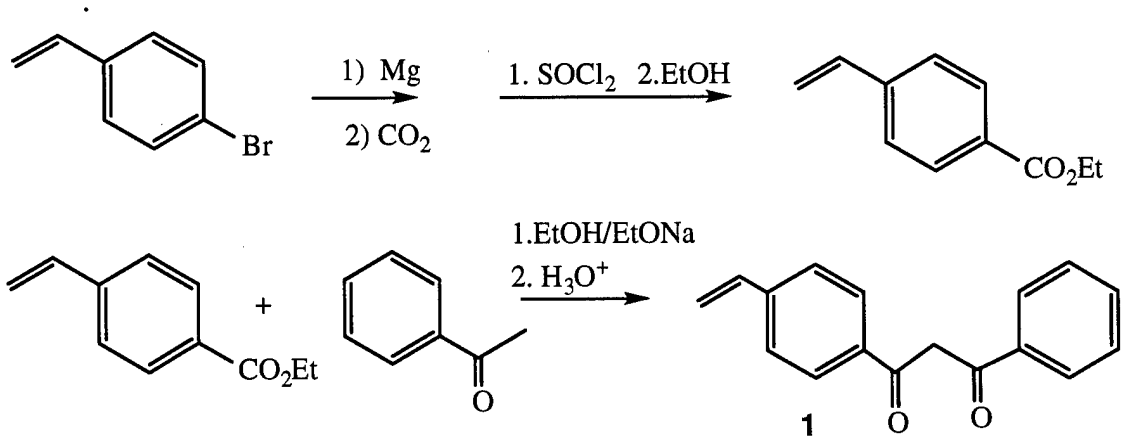
The synthesis of p-vinylbenzoylacetophenone (monomer **1**) starts with the Friedel Crafts acylation of 2-chloroethylbenzene,**3**, with acetyl chloride to give **4**[1] and is followed by a base mediated elimination of **4** to give 4-acetylstyrene (**5**).[2,] The last step of the synthesis involves the sodium hydride mediated Claisen condensation of **5** with

ethylbenzoate.[3,4] It is necessary to have an excess of ethylbenzoate as the competing aldol (self) condensation of the 4-acetylstyrene must be avoided.



Scheme-1. Synthesis of *p*-vinylbenzoylacetophenone

It should be pointed out that the reaction product in this case is not monomer **1** but rather its enolate anion as **1** contains a highly acidic hydrogen (pKa between 9 and11) that is readily removed under the basic reaction conditions. The monomer itself is obtained by protonation under mildly acidic conditions.



Scheme 2. Alternative synthesis of *p*-vinylbenzoylacetophenone

An alternate synthesis of **1** is shown in Scheme 2. Starting with 4-bromostyrene the carboxylation of the corresponding Grignard gives the 4-vinylbenzoic acid that is esterified and reacted with acetophenone to give the desired monomer. However, the second scheme was abandoned as the second procedure required the synthetically expensive 4-vinylethylbenzoate in excess.

The reported synthetic methods were improved as follows:
1. The use of 1,2 dichloroethane greatly improved the yield of step (1). 2. The elimination (step 2) required refluxing methanol rather than the reported 0 ^{0}C. 3. The third step was found to give better yields when benzene was used as solvent. The synthesis of vinyl monomer,**1** ,was optimized to give an isolated overall yield of about 35 percent from the starting products. The detailed synthetic procedures are given below.

Acetylation of (2-chloroethyl)benzene (eqn. 1). A solution of acetyl chloride (0.10 mol) and aluminum chloride (0.05 mol) in dry 1,2-dichloroethane was added to a solution of 2-chloroethylbenzene (0.04 mol) in the same solvent. After a few minutes reaction, the solution was poured into ice water. The organic phase was washed with sodium hydroxide solution and water. After drying over sodium sulfate, the solvent was removed under vacuum. The residue(yield was 80%) was not purified further.

Dehydrohalogenation of 4,(eqn. 2). Three grams of 2-(p-acetylphenyl)ethyl chloride was dissolved in 40 ml methanol and 2 grams of KOH was added. After the mixture was refluxed for one hour the solution was cooled to room temperature and the KCl precipitate was removed by filtration. Methanol was removed on rotary evaporator and 50 ml of chloroform was added. The organic phase was washed with dilute hydrochloric acid and water. After drying over sodium sulfate chloroform was removed on rotary evaporator. The final product was obtained by vacuum distillation (CuCl was added to prevent thermal polymerization of 4-acetylstyrene) as a colorless liquid, b.p. 75 °C/0.3 mm Hg. Yield was 80%.

Claisen Condensation (eqn. 3). To a three-neck flask were added 7.5 g ethyl benzoate (0.05 mol), 1.13 g NaH (0.046 mol) and 50 ml dry benzene. The mixture was kept under argon and heated to reflux. A solution of 3.30 g of 4-acetylstyrene (0.023 mol) in 40ml benzene was added dropwise over a period of 3-4 hours. After the addition was complete, the mixture was allowed to reflux for an additional three hours. As the reaction continued an orange sediment of the sodium enolate appeared. After the mixture was cooled to room temperature, the mixture was acidified by addition of 1.0 M. sulfuric acid and the mixture was stirred vigorously for several minutes until the sodium enolate precipitate disappeared. The organic phase was separated and washed with water, dilute sodium bicarbonate solution and water. After drying over sodium sulfate, benzene was removed on rotary evaporator. The viscous residue was placed in refrigerator overnight and solidified. After filtration the solid was washed with methanol. Upon placing the filtrate in the refrigerator overnight additional solid appeared that was separated by filtration. The combined solids were recrystallized twice from methanol to give light yellow crystals (yield was 50%; m.p.= 86.5-87.0 ^{0}C). The proton NMR spectrum showed the expected resonances in the correct relative proportions and did not indicate the presence of impurities. Proton NMR ($CDCl_3$): 5.45, 5.94 and 6.85 (3H vinyl protons), 6.93 (s, 1H

of CH enolate) 7.5-8.2 (9H, m, phenyl protons) and 12.2 (s, 1H, OH enolate). The mass spectrum was also in accord with the structure of **1** (MS: 251(M^+), 221, 147, 105,77). The overall yield of **1** from starting products was 35 percent.

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